

THE ROLE OF IN SITU MEASURED FREE RADICALS
IN THE KINETICS AND MECHANISM OF THE HYDROLIQUEFACTION
OF POWHATAN #5 COAL

by

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The possible role of free radicals in the mechanism of coal liquefaction has been a subject of much interest to coal researchers (1-4). Free radicals have been measured in coals and treated coals for many years (5) and more recently have been measured in coal liquefaction fractions (6, 7) and slurries after liquefaction (8, 9). We have recently developed the capability to measure free radical concentrations in coal liquefaction processes from a few minutes after the slurry has reached reaction temperature. The results of in situ free radical measurements on Powhatan #5 coal have been reported (10-13). We report here the liquefaction yields from these and parallel autoclave studies, the statistical model used to analyze both the free radical concentrations and the yields as well as a kinetic model of coal liquefaction in which measured free radicals are included as intermediates.

The experimental details have been given in earlier papers (10). Powhatan #5 coal was used throughout these experiments. The in situ measurement of free radicals was done in a specially fabricated high-temperature, high-pressure ESR cavity (14, 15). A batch autoclave system was used when larger amounts of sample were desired for extensive analysis of the liquefaction products. Oil, asphaltene, and preasphaltene yields were determined by exhaustive Soxhlet extraction of the liquefaction slurry from both in situ cavity and the shaken autoclave.

The results of the in situ free radical measurements on Powhatan #5 liquefied under a wide variety of conditions have been reported (11). Temperature, solvent, and residence time were found to be the most important variables affecting the free radical concentration during the liquefaction of Powhatan #5 coal. Gas type, pressure, and heating time were found to be less important. These results have been explained in terms of the hydrogen-donating ability (hydroaromatic content) of the solvents and the larger quantity of energy available for bond breakage at higher temperatures. The various effects of the variables on the spin concentration during liquefaction have been quantified by use of a statistical model (13).

Liquefaction yield was determined in about one hundred in situ ESR and autoclave experiments. In the tetralin solvent experiments, conversion increases with time for all temperatures up to 480°C where a slight decrease is noted at the longest reaction time, 40 minutes. Oil yields increase with time for all reaction temperatures. Oil is the predominant component of the

conversion yield at all temperatures greater than 400°C. At 400°C, the yields of all of the components are similar. As can be seen in Figure 1, preasphaltene yield decreases with time, and asphaltene yield decreases slightly. It would appear, since conversion does not increase significantly between 10 and 40 minutes at 450 or 460° and decreases at 480°C, that the oil is produced from the preasphaltene or asphaltene fractions, as has been suggested in the literature (16). When naphthalene is used as the liquefaction solvent, overall conversion, asphaltene, and oil yields are found to increase with reaction times for all of the temperatures, although somewhat more sharply at the lower temperatures between 3 and 10 minutes reaction time. Preasphaltene yields decrease somewhat with reaction time at 440°C and above. It would appear that at the lower temperatures, reaction is relatively incomplete and that more time is needed for product formation.

When SRC-II heavy distillate is used as the solvent, overall conversion increases with time at 400°C, is fairly constant with time at 425 and 440°C, decreases with time at 450°C, and decreases sharply with time at 460 and 480°C. Below 440°C this increased reaction time favors conversion, at 450° and above, coking reactions are favored at longer residence times. Longer residence times increase oil production at 440°C and lower temperatures but decrease oil production at higher temperatures.

As a reference for the liquefaction data obtained with the solvents, the yields were measured from the liquefaction of Powhatan #5 coal without solvent for 40 minutes in 1600 psig of H₂ gas. The overall conversion is low, about 22%, with the vast majority of it being oil. A blank run using SRC-II heavy distillate was done to check for thermal degradation of the solvent. After shaking for 40 minutes at 460°C and with 1600 psig H₂, more than 98% of the SRC-II heavy distillate was pentane soluble.

The Severity Parameter. Noting the apparent trade-off between time and temperature, i.e., long residence times at lower temperature produce yields equivalent to short residence times at higher temperatures in many cases, the concept of "reaction severity" as a combination of these variables appeared to be a potentially useful parameter. Severity, the combination of residence time and temperature, is arbitrarily defined as the sum of 2 times the residence time in minutes and the temperature in degrees centigrade minus 400. For example, 440°C and 40 minute residence time would be a severity of $2 \times 40 + (440 - 400)$ or 120.

Figures 2 and 3 are plots of overall conversion as a function of severity for the three solvents. For the tetralin experiments (Figure 2), conversion increases as a function of severity with evidence of decrease only at the highest level of severity. The naphthalene data show similar behavior. The SHD liquefaction conversion data, however, show a distinct downturn in conversion at severity levels over 100, indicating that retrogressive or coking-type reactions are important at longer residence time and at higher temperatures (Figure 3). There appears to be a broad maximum in conversion at intermediate severity when SHD is the liquefaction solvent as opposed to tetralin or naphthalene. Oil yield and asphaltene yield were also analyzed as a function of severity and will be discussed in the talk.

Correlative Models for Conversion. The liquefaction data from these experiments were also analyzed by a linear regression model. The yields were expressed in terms of oils, oils + asphaltenes, and total conversion (oils + asphaltenes + preasphaltenes). The yields follow an exponential growth or decay pattern. The model contained exponential time, temperature, and pressure terms essentially the same as those terms described in a previous paper (13). The analytic form of each term in the model is shown in Table I. It is important to point out that each term involves an interaction between at least two variables.

The overall statistics show that solvent is quite important and ranks second to residence time in significance. The solvent * time interaction time (ZTIME * SOLVENT) generally ranks as the most significant interaction in the model. The time * temperature terms (ZT or ZTT) are significant for the oil and total conversion (conv) models. These terms are not significant at all for the ASPH (asphaltenes + oils) model. Other variables such as gas type and pressure (ZTIME * GAS, ZP, ZTP) never achieve significance. This is consistent with the previous findings for the measured spin concentration model (13).

Covariance Model of Free Radicals and Total Conversion. Based on the strong similarity in the functional forms of the radical and conversion models, we have determined models for the various lumped conversions in terms of spin concentration (CSCON) and various interactions between spin concentration and solvent, gas, temperature, and CSCON itself. Each yield (oil, asphaltenes + oil, total conversion) is expressed in the following form:

$$I +$$

$$\text{Yield} = C_1 * \text{CSCON} + C_2 * \text{CSCON} * \text{SOLVENT} + C_3 * \text{CSCON} * \text{GAS}$$

$$+ C_4 * \text{CSCON} * \text{DTEMP} + C_5 * \text{CSCON} * \text{CSCON}$$

where I is an intercept term, CSCON is the corrected spin concentration $\times 10^{18}$, DTEMP is temperature, and SOLVENT and GAS refer to solvent and gas types.

The statistics (Table II) show that CSCON is the most significant single variable. However, non-linear CSCON^2 and $\text{CSCON} * \text{SOLVENT}$ interaction effects are also quite important. The spin concentration term alone accounts for a large fraction of the overall sum of squared yield values. It should be noted that CSCON is not an independent variable, but depends on solvent, gas, temperature, and time. The correlation models show that the growth of the spin concentration correlates very strongly with the observed yield growth curves. By statistical techniques, it is possible to determine more fundamental reaction rate expressions relating spin concentrations to products, to map out plausible reaction paths, and determine the rate constants.

Development of Correlative Models for Each Conversion Species. The first step was to determine correlation models in terms of the four solubility fraction products: oils, asphaltenes, preasphaltenes, and THF insolubles.

Essentially the same terms were used to correlate these products as were used in the lumped models. The statistics show that the time * solvent and time * temperature interactions are significant. The interactions between temperature and residence time are clearly shown by means of contour plots in which spin concentration, oil yield, or total conversion levels are plotted with temperature (400 to 480°C) along the vertical axis and residence time (RTIME) (0 to 60 minutes) along the horizontal axis (Figure 4).

Methodology for Kinetics. Models based on fundamental kinetics are specific differential material balances of the yields which, when integrated, describe the formation of the products with time. In this work a general differential "material balance" form is proposed and the rate constants are determined by linear stepwise regression techniques. A series of reactions was determined at each temperature and solvent system which was consistent with overall material balance requirements.

The models show that coal breaks up into radicals which are present in the various solubility fractions. The radicals are stabilized or capped by reacting with various other radical and non-radical species or by transfer of hydrogen to or from the solvent. The solvent is not explicitly present in these reactions as a participant in the hydrogen-transfer pathways. Three classes of reactions are identified: progressive, disproportionation, and retrogressive reactions.

Mechanistic Implications. The progression of reaction from coal to preasphaltenes to asphaltenes to oils has been shown not to be kinetically related to the measurable free radical concentration. By contrast, the retrogressive reactions are kinetically determined by the steady state free radical content with the importance of these reactions increasing with temperature. The hydrogen donation power of the solvent has an impact on these reactions by decreasing the steady state concentration of the free radicals and favoring the competing conversion reactions which are not kinetically dependent upon measurable free radicals. Many conversion reactions are probably occurring via a free radical mechanism, however, the lifetime of these radicals may be too short to build up a concentration large enough to be observed over the naturally occurring radical concentration in coal. The reaction of Powhatan #5 coal in tetralin at 400°C produces a reasonable level of conversion (50% or more) without a measurable change in free radical concentration relative to that of the unheated coal. Such a non-observation of additional, thermally-formed free radicals does not rule out a free radical mechanism in which the radicals are relatively short lived ($t_{1/2} \sim 10$ sec).

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Figure 1
Yields vs Residence Time
Tetralin Solvent 480°C Autoclave Reactor

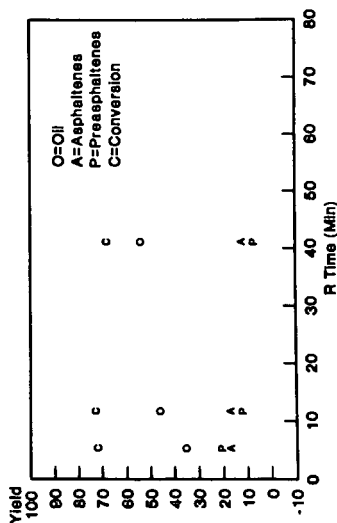


Figure 3
Conversion vs Severity
SRC II HD Solvent

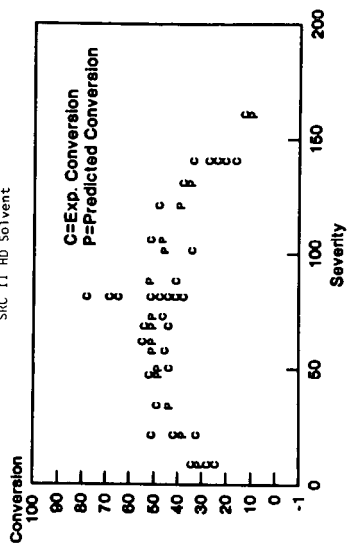


Figure 2
Conversion vs Severity
Tetralin Solvent

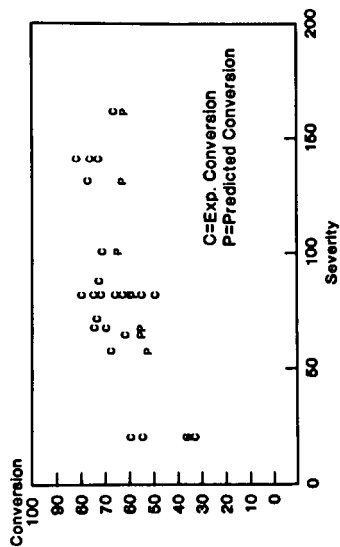
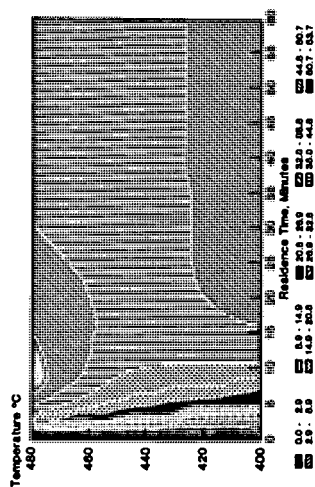


Figure 4
Contour Plot of Conversion as a Function
of Temperature and Residence Time
Napthalene Solvent



DEFINITION OF TERMS IN CORRELATION MODELS FOR LUMPED AND INDIVIDUAL PRODUCT YIELDS

Continuous Variables:

TIME	Elapsed time in minutes
INTIME	Average elapsed time
TEMPK	Reaction temperature, °K
PRESS	Pressure in psig
MPRESS	Average pressure

CORRELATIVE MODELS FOR LUMPED PRODUCTS IN TERMS OF SPIN CONCENTRATION - ANALYSIS OF VARIANCE

Relative Ranking of Importance of Model Terms by Type I S.S. Statistical Text

Model Term-Variables		Type I S.S.		Contribution		Significance	
		011	ASPH	011	ASPH	011	ASPH
CSCON	Spin Conc.	17504	38334	53569	.808	.843	.797
CSCON*	Spin Conc.*						.0001
SOLVENT	Solvent	2868	3566	5550	.132	.078	.083
CSCONZ	Spin Conc.*						.0001
CSCON	Spin Conc.	1066	3118	6699	.049	.069	.100
CSCON*GAS	Spin Conc.*Gas	148	2334	600	.007	.051	.009
CSCON	Spin Conc.*						.0001
OTEMP	Temperature	82.4	204.3	816	.004	.004	.0121
Total							.1973
Total Model	Type I S.S.	21659	45456	67204			.1270
Total	Corrected S.S.	27481	55681	86556			.0275
Error	S.S.	5782	10206	19323			
Error	R ²	.79	.82	.78			
Total Number of Points 124							
Yield = Intercept + Sum of Regression Coefficient * Model Term							

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